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Conformational probes in study of glassy polymers

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Abstract

This work is devoted to development of FTIR spectroscopic method of conformational probes in glassy polymers. A new approach is employed to model the freezing of conformational transitions in probe molecules in glassy polymers. This method is based on introducing small molecules (probes) in a polymer and following conformational dynamics in the probe molecules at different temperatures. For each polymer-probe system, freezing of conformational transitions is observed by FTIR at a certain individual temperature, T_f. A linear correlation between the freezing temperature T_f of conformational transitions of probe molecules and the size of rotational fragments of probe molecules is observed. The magnitude of T_f increases with the size of rotational fragments of the probe molecules and decreases with the free volume fraction of the studied polymers. The obtained results were interpreted in terms of existing "mobile" and "fixed" free volume entities in glassy polymers. The new representations about the processes occurring in polymeric matrices at T_f are given. Finally, relaxation transitions observed in the polymers at the temperatures T_f were assigned to certain types of molecular mobility of their lateral groups.

Keywords: Free volume; Glassy polymers; Conformational probes

1. Introduction

Many physical properties and phenomena in materials are due to free volume in polymers (at temperatures lower than the glass transition temperature of a polymer, T_g, in particular). The simulation of transport in membranes and establishment of mutual connection of transport parameters with the polymer structure require deep understanding of the effect of structure's elements on the realized free volume. The transport of low-molecular-weight substances through polymers is a complex process, which is controlled by the polymer free volume and the polymer-penetrant molecular interactions. Free volume is the fraction of the volume not occupied by the polymer. This concept has found uses in discussing physical properties such as viscosity, diffusion in liquids, viscoelasticity, electrical conductivity, the glass transition and plastic yielding. For any polymer, the free volume can be characterized by the total free volume magnitude, its size distribution and free volume moieties' dynamics. Fractional free volume, *FFV* [cm^3 of free volume/cm^3 of polymer], is commonly used to characterize the efficiency of chain packing and is widely used as a correlating parameter for polymer permeation properties:

$$FFV = \frac{1/\rho - 1.3V_W}{1/\rho}, \quad (1)$$

where V_W is the van der Waals volume of the repeat unit of the polymer, ρ is the polymer density [1,2].

There is a distribution of the free volume over the size of the free volume moieties, which are also referred to as "holes" and "microcavities". Local dynamics of polymer molecules allows the free volume elements to be transported and the penetrant molecules to be diffused. Different regions of free volume distribution take part in different processes of mass transfer. In particular, for viscous flow and deformation, probably, the "right wing" of this

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